

A Constrained Molecular Dynamics Study of Potassium Chloride Ion Pair in Water – acetone Mixtures

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ABSTRACT

Constrained molecular dynamics simulations have been performed for K^+ - Cl^- ion pair in mixtures of water and acetone for various compositions with $x_{\text{acetone}} = 0.20, 0.40, 0.50, 0.60$ and 0.80 . The potential of mean force (PMF) curves obtained for all the mixtures provide information about existence and stabilities of contact ion pair (CIP), solvent assisted ion pair (SAIP) and solvent separated ion pair (SSIP) in the solution. The trajectories done with various starting configurations and the resulting average residence times support the PMF. The PMF obtained for the K^+ - Cl^- ion pair in pure acetone shows a deep minimum around 3.0 \AA suggesting that the ion pair prefers to remain in CIP state.

Keywords: potential of mean force; contact ion pair; solvent assisted ion pair; solvent separated ion pair.

1. INTRODUCTION

The nature of interaction of ions with solvents has been the subject matter of several studies^{1, 2}. Various methods such as constrained molecular dynamics (MD)^{3, 4} have been used to investigate the solvation structure and dynamics of ion pairs in solvents and mixture of solvents⁵⁻¹⁰. Many important chemical changes occur in solution state where solvents play significant role. Polar solvents such as water and acetone are used in large number of

reactions and therefore it is necessary to have understanding of solvation structure of ion pairs in polar solvents and their mixtures.

Ion pairs have significant influence on the nature of reactions in solution media such as solvolysis and catalysis. In any solvolysis reaction the complete ionization of stable solute molecules involves different ion pair states known as contact ion pair (CIP) and the solvent separated ion pair (SSIP). In between the two states, exist a solvent assisted ion pair (SAIP) state. CIP

and SAIP/SSIP are clearly defined in the pmf curves obtained by constrained molecular dynamics (MD) simulations.

KCl is also an electrolyte of particular interest because of wide range of its applications in chemistry and its biological significance. Acetone has widespread application as solvent. In the laboratory, it is used as a polar aprotic solvent in a variety of organic reactions. The ion solvation and ion pairing study of various alkali salts in this commercially important mixture has not been fully explored so far. An effort to calculate the PMF values at different concentrations and related solvation studies of alkali salts needs to be done in these mixtures. In the present article, pmf curves for K^+ - Cl^- ion pairs in mixtures of water and acetone for various compositions with $x_{\text{acetone}} = 0.20, 0.40, 0.50, 0.60$ and 0.80 have been obtained to explain the solvation of ion pairs. All the calculations have been done at Molecular Dynamics Laboratory in the Department of Chemistry, IIT – Bombay.

The methodology and computational details are briefly described in section 2; results and discussion in section 3, and conclusions are summarized in section 4.

2. THE METHODOLOGY AND COMPUTATIONAL DETAILS

All the calculations have been done at Molecular Dynamics Laboratory in the Department of Chemistry, IIT – Bombay using Fortran 77 program developed by Tembe and Co-worker.

The constrained MD methodology has been used in the simulations. The method involves MD simulations of the system consisting of the ions and the solvent

molecules in which all the intra solvent atom-atom separation are held constant. Also the ion – ion separation is kept fixed. This was achieved by using the SHAKE algorithm¹¹. The long range interactions were computed using the reaction field technique¹². The equations of motion were solved numerically using the Verlet algorithm¹³ using a time step of 0.1 fs. We have observed that with larger time steps, it is often difficult to obtain equilibration. For each of the inter ionic separations of 2.0 Å to 8.0 Å the system was equilibrated for 100 ps and followed by production period of 1 ns.

For water, we have used SPCE¹⁴ model whereas, acetone molecules are modeled by the OPLS potential model of Jorgensen et al¹⁵, which comprises of two methyl, one carbon, and one oxygen sites. Each methyl group is considered as single interaction site and thus the hydrogen atoms of acetone are not considered separately. The K^+ and Cl^- solutes are considered as charged Lennard-Jones particles¹⁶⁻²¹. The values of the Lennard-Jones and electrostatic inter-action potential parameters of different atomic sites of water and acetone and also of solute particles are summarized in Table 1.

Table 1. Force field parameters for Acetone, water and potassium chloride Values of Lennard-Jones and electrostatic interaction potential parameters. e represents the magnitude of electronic charge.

Atom/ ion	$\sigma / (\text{\AA})$	$\epsilon / (\text{k J/mole})$	Charge/ e
Water- O	3.166	0.65060	- 0.8476
Water – H	0.000	0.00000	+0.4238
Acetone – C	3.750	0.43632	+0.300
Acetone – CH3	3.910	0.66944	+0.062
Acetone – O	2.960	0.87864	- 0.424
K^+	3.250	52.1619	+1.000
Cl^-	3.785	52.1619	-1.000

The details of the chosen solvent mixtures are given in Table 2.

Table 2. Solvent 1=acetone; Solvent 2 = water; x_i = Mole fraction of solvent I, n_i = number of molecules of solvent i in the cubic simulation cell of edge length L; ρ = Density at 298 K; ϵ = Dielectric constant. Box length for each composition =25.000 Å (NVT ensemble)

Com-position	x_1	x_2	n_1	n_2	ρ (g/cm ³)	ϵ
1	0.20	0.80	67	266	0.9199	66.98
2	0.40	0.60	97	145	0.8741	54.60
3	0.50	0.50	105	105	0.8534	48.22
4	0.60	0.40	112	75	0.8371	41.80
5	0.80	0.20	122	20	0.8073	29.62

In order to simulate the K⁺ and Cl⁻ ions in the pure acetone solvent, the two ions were placed in a cubic simulation box of box length 25.000 Å (NVT ensemble) containing 128 acetone molecules. The density of system is 0.7846 g/cm³ at 298 K and a dielectric constant of 19.10

2.1. The Potential Model

The solvent – solvent, solute – solvent and solute – solute interactions are taken to be pair wise additive and comprise of Lennard – Jones and Coulombic terms. The site – site potential has been taken as

$$U_{\alpha\beta}(r) = \left[\frac{A_{\alpha\beta}}{r^{12}} - \frac{C_{\alpha\beta}}{r^6} \right] + \frac{q_{\alpha}q_{\beta}}{r} \quad (1)$$

Where r is the site – site separation in Å, α and β are the interaction sites on different molecules. q_{α} and q_{β} are the charges located at sites α and β respectively.

$$A_{\alpha\beta} = 4\epsilon_{\alpha\beta}(\sigma_{\alpha\beta})^{12} \quad (2)$$

$$B_{\alpha\beta} = 4\epsilon_{\alpha\beta}(\sigma_{\alpha\beta})^6 \quad (3)$$

where $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are the energy and distance parameters in Lennard – Jones potential.

$$\sigma_{\alpha\beta} = (\sigma_{\alpha\alpha} + \sigma_{\beta\beta})/2 \quad (4)$$

$$\epsilon_{\alpha\beta} = (\epsilon_{\alpha\alpha}\epsilon_{\beta\beta})^{1/2} \quad (5)$$

For the system consisting of two ions (A, B) and N solvent molecules, the total mean force between the ions is the sum of the direct (bare) ion – ion force, $F_d(r)$ and the solvent contribution, $\Delta F(r)$. That is,

$$F(r) = F_d(r) + \Delta F(r) \quad (6)$$

The potential of mean force, $W(r)$ of the ion pair in the presence of the solvent can be calculated as

$$W(r) = - \int_{r_0}^r F(r) dr = W(r_0) - \int_{r_0}^r F(r) dr \quad (7)$$

The choice of $W(r_0)$ is required to be done in such a way that calculated mean force potential matches the macroscopic Coulombic potential at long distances

$$W(r_0) = \frac{q_i q_j}{r_0 \epsilon} \quad (8)$$

where q_i is the charge on the i^{th} ion and ϵ is the dielectric constant of the solvent. It has been found that ion – ion PMFs for the solvent compositions studied are not sensitive to the choice of r_0 at a distance greater than 8.0 Å.

The problem of surface effects is effectively removed by implementing periodic boundary conditions.

3. RESULTS AND DISCUSSION

3.1. The Potential of Mean Force

The ion – ion PMFs, $W(r)$, for all the solvent compositions have been obtained by direct integration of the total force, $F(r)$, according to eqn. 7 given in sec 2.1, taking $r_0 = 8.0 \text{ \AA}$ and are shown in the fig.1

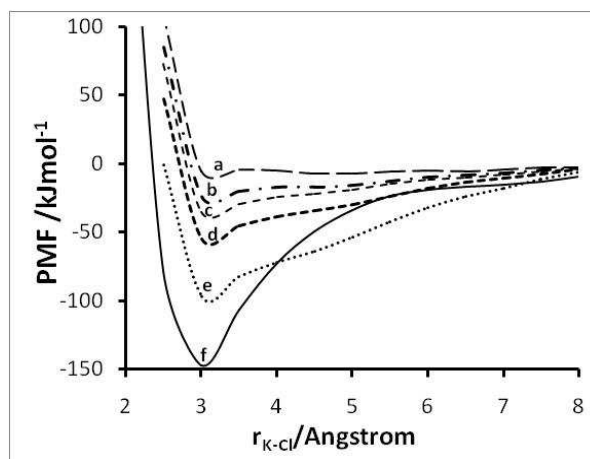


Fig. 1. Potential of mean force for $K^+ - Cl^-$ ion pair in water - acetone mixture with (a) $x_{\text{acetone}} = 0.20$ (b) $x_{\text{acetone}} = 0.40$ (c) $x_{\text{acetone}} = 0.50$ (d) $x_{\text{acetone}} = 0.60$ (e) $x_{\text{acetone}} = 0.80$ and (f) in pure acetone.

The locations of first minimum corresponding to CIP, first maximum corresponding to transition state and second minimum corresponding to SAIP are summarized in the table 3.

Table 3. The characteristics of the $K^+ - Cl^-$ PMF curves for mixtures of water- acetone

x_{acetone}	First minimum* (Å)	Depth of first minimum kJ/mol	First maximum (Å)	Height of First maximum kJ/mol	Second minimum (Å)	Depth of second minimum kJ/mol
0.20	2.8	-5.54	3.9	-4.94	5.2	-5.81
0.40	2.8	-24.01	4.1	-17.14	5.0	-15.92
0.50	2.8	-35.21	4.2	-24.60	5.0	-20.50
0.60	2.8	-54.90	---	---	---	---
0.80	2.8	-96.73	---	---	---	---
1.00	2.8	-147.13	---	---	---	---

* The location of the minima have been taken from the dynamical trajectories

The PMF curve obtained for KCl ion pair in acetone- water mixture shows presence of stable CIPs in all the compositions. The curves for compositions

with $x_{\text{acetone}} > 0.20$ also suggest presence of relatively less stable SAIPs. The stabilities of CIPs changes with change in mole fraction of acetone. In the mixture having

$x_{\text{acetone}}=0.20$, the stabilities of both CIP and SAIP is comparable which appears at 2.80 Å and 5.2 Å respectively. The nature of PMF in this composition suggests a transition from the CIP to SSIP through a small barrier. With increase in mole fraction of acetone, the depth for CIPs increases and CIPs becomes more stable. In the mixtures with $x_{\text{acetone}} > 0.50$, the SAIPs cease to exist. The increase in depth of minimum for CIP is found to change drastically with change in mixture composition from $x_{\text{acetone}}=0.80$ to $x_{\text{acetone}}=1.00$ i.e. pure acetone. The deep in

PMF curve for KCl ion pair in pure acetone suggest that the CIP is very stable and the only species that exist.

The derived PMF curves are strongly supported by dynamical ion – ion trajectories of the pair using respective auxiliary MD simulation programmes. The calculation of residence time provides additional support to the PMF curves. The testing of the PMFs using the dynamical trajectories of the ion pair is discussed below.

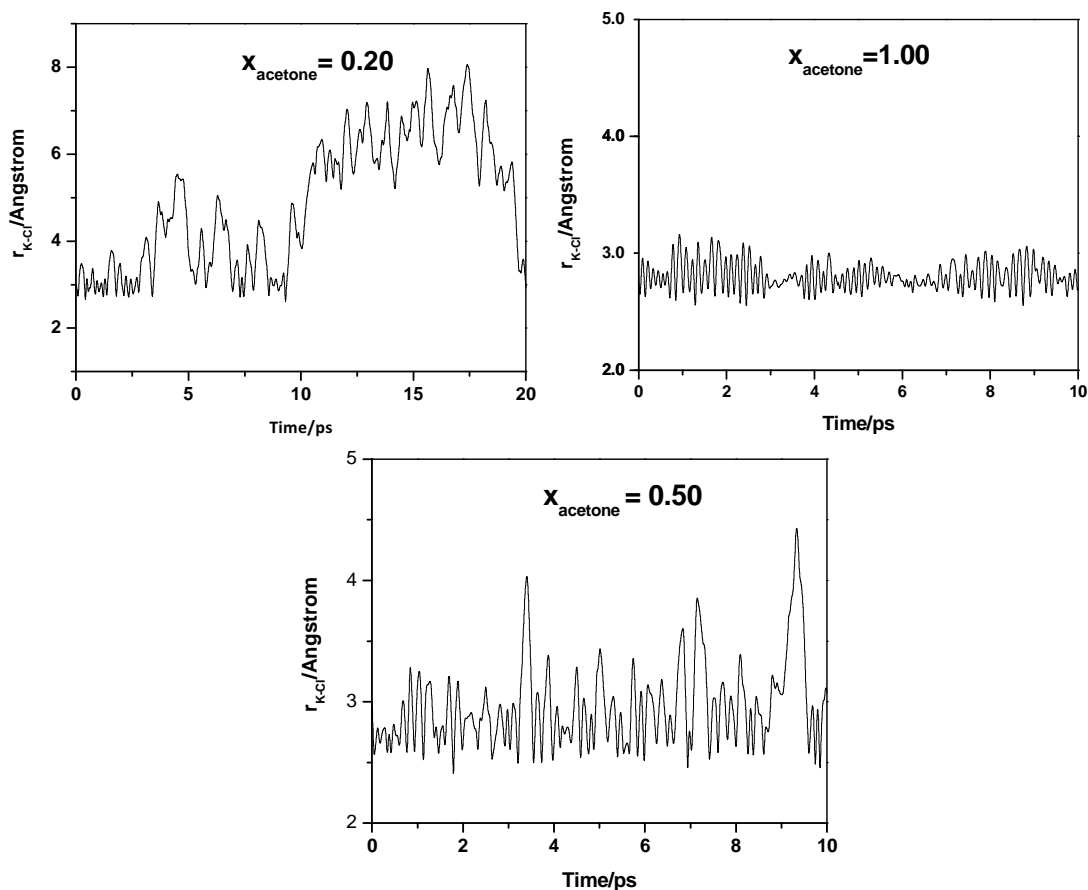


Fig. 2. Representative Trajectories of $K^+ - Cl^-$ ion pair in water – acetone mixtures with starting ion – ion separation of 3.0 Å for each compositions.

3.2. Dynamical Trajectories of ion pair/s

The nature of potentials of mean force for the ion pair is confirmed by studying the dynamical trajectories of the ion pair initiated at various ion – ion separation. A long MD simulations on the system was carried out by releasing the constraint on the ion pair at time $t = 0$, and then calculating the ion – ion separation vector at each time step. The interaction of solvent molecules with each other and with solute ions contributes to the dynamics of

the ion pair. For each of the mixture composition, several interionic separations have been chosen as the starting ion – ion distance and each of the ion – ion trajectories are followed up to 20ps. In the figs. 2-3, the representative trajectories have been shown. In each of the starting ion – ion distances shown in these figures, several equilibrated configurations have been generated for the systems, but only a few representative dynamical trajectories are displayed.

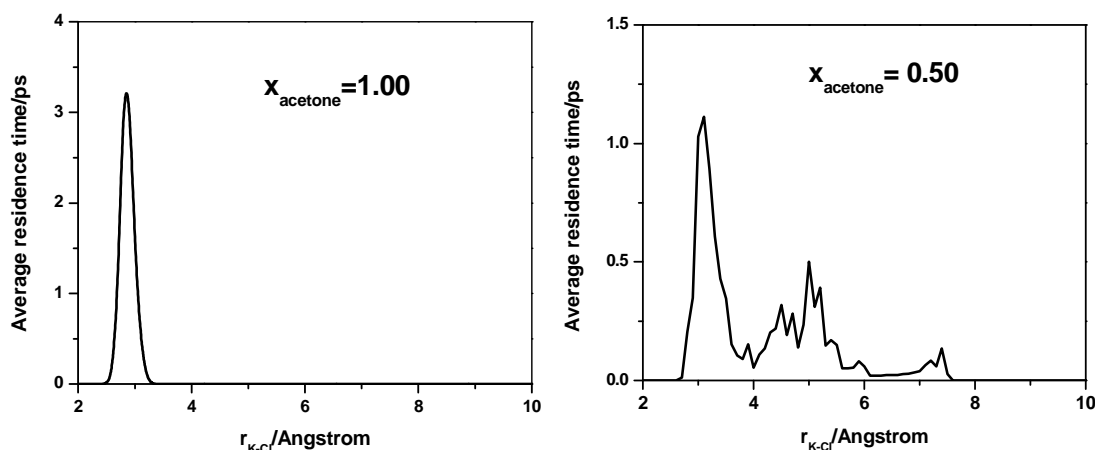


Fig. 3. Representative average residence times of $K^+ - Cl^-$ ion pair in pure acetone for 25 ps with starting ion - ion separation of 3.0 Å for each compositions.

The trajectories starting at $r_{K^+ - Cl^-} = 2.0$ Å, tends to settle around 3.0 Å for about 60% of time for $x_{\text{acetone}} = 0.20$ and for about 75% of time for $x_{\text{acetone}} = 0.40$ thereby confirming presence of CIP at 2.8 Å. It then oscillates between 4.0 Å to 5.5 Å indicating a shallow solvent shared ion pair minimum around 5.0 Å for both the compositions. Similar behavior is observed for trajectories starting at 4.0 Å, 5.0 Å, 6.0 Å and 7.0 Å. The trajectory starting at 3.0 Å, remain

around 3.0 Å for about 80% of time and also shows intermittent oscillation between 3.5 Å to 5.0 Å, confirming the presence of stable CIP and a shallow minimum for SAIP.

For $x_{\text{acetone}} = 0.50$, the behavior of trajectories are similar to those observed for $x_{\text{acetone}} = 0.40$. For mixture compositions with $x_{\text{acetone}} > 0.50$, the trajectories starting at various inter ionic separations converges around 3.0 Å, confirming the presence of very stable CIP.

The dynamical trajectories of the KCl ion pair in pure acetone, initiated at various ion – ion separation resides at 2.8 Å suggesting a very stable CIP.

4. SUMMARY AND CONCLUSIONS

Constrained MD simulations have been performed on the K^+ - Cl^- ion pair in the water- acetone mixtures with compositions ranging from $x_{\text{acetone}} = 0.2$ to $x_{\text{acetone}} = 0.8$. Simulations studies have also been done for these ion pairs in pure acetone as solvent. The PMF has been calculated and the ion pair and solvation structure studies have been done. The derived potentials of mean force (PMF) for the ion pair suggest the existence of stable contact ion pairs (CIPs) in all the mixtures. The PMF curve for mixture compositions of $x_{\text{acetone}} = 0.2$ to $x_{\text{acetone}} = 0.50$ also indicates the presence of shallow solvent assisted ion pairs (SAIPs). The region beyond 6 Å for all the compositions does not provide any evidence of solvent separated ion pairs (SSIPs). The derived PMF curves are strongly supported by dynamical ion – ion trajectories of the pair performed using auxiliary MD simulation programmes.

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